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RESEARCH ARTICLE

Emission and distribution of PCDD/Fs, chlorobenzenes, chlorophenols, and PAHs from stack gas of a fluidized bed and a stoker waste incinerator in China

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Abstract The concentrations, homologue, and congener profiles, as well as the gas/particle distribution of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), chlorobenzenes (CBzs), chlorophenols (CPhs), and polyaromatic hydrocarbons (PAHs) from stack gas of two different municipal solid waste incinerators in China, were characterized. The incinerators were a stoker furnace incinerator equipped with the advanced air pollution control device (APCD) and a common circulating fluidized bed (CFB) furnace. The concentration of PCDD/Fs in the stack gas of the stoker incinerator ranged 0.011–0.109 ng international toxic equivalent factor (I-TEQ)/Nm^3 and was below the current limit for PCDD/F emissions from the municipal solid waste incinerators (MSWIs) in China (0.1 ng I-TEQ/Nm^3) in most of the cases. Moreover, the concentration of PCDD/Fs in the stack gas of the stoker incinerator was significantly lower than that of the CFB incinerator (0.734 to 24.6 ng I-TEQ/Nm^3). In both incinerators, the majority of the total PCDD/F emissions (above 90%) ended up in the gas phase. 2,3,4,7,8-PeCDF, which occupied 24.3–43.6 and 32.5–75.6% of I-TEQ contribution in MSWIs A and B, respectively, was the most abundant congener. However, different types of incinerators and APCDs induced different congener and homologue distributions. The total concentration of CBzs from the stoker incinerator (0.05–3.2 μg/Nm^3) was also much lower than that formed from the CFB incinerator (10.9–75.2 μg/Nm^3). The phase distribution of CBzs followed the same pattern as with the PCDD/Fs. Moreover, the emission level of CBz was 100–1000 times higher than that of the PCDD/Fs, which determines the applicability of CBzs as indicators of PCDD/F emissions. High correlations between the emission concentrations of PCDD/Fs, TeCBz, and PCBz in specific ranges were revealed. Furthermore, high concentrations of CPhs (0.6–141.0 μg/Nm^3) and PAHs (148.6–4986.5 μg/Nm^3) were detected in the stack gases of MSWI B. In some cases, the concentrations were as high as the concentrations in the fumes exiting the boiler of one foreign stoker without flue gas purification indicating the abundance of CPh and PAH emissions in the stack gas of waste incinerators.

Keywords Waste incineration · Stack sampling · Polychlorinated dibenzo-*p*-dioxin · Polychlorinated dibenzofuran · Chlorinated pollutants · Polyaromatic hydrocarbons

Introduction

The amount of municipal solid waste in China greatly increases with the growth of the population and increase of GDP. The amount of municipal solid waste (MSW) generated increased from 158.048 million t in 2010 to 178.602 million t in 2014 (National Bureau of Statistics of China 2011, 2015). The number of MSW incineration plants also increases (up to 188 plants in 2014), as this disposal method is seen the most efficient (National Bureau of Statistics of China 2011; National Bureau of Statistics of China 2015). The daily capacity of MSW incineration expanded to 1859.57 million t in 2015 from 849.40 million t in 2010 (National Bureau of Statistics of China 2011, 2015). Furthermore, 121 incineration plants are under construction while 106 plants are being planned. By the end of 2020, the municipal solid waste

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incinerator (MSWI) plants are expected to treat more than 50% of the total waste with the capacity of MSWI plants equal to 1 million t per day (National Development and Reform Commission 2016).

Although incineration is proposed as an environmentally benign alternative to MSW landfilling, formation of air-borne emissions, such as SO_2, NO_x, particulate matters (PM), and more importantly polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), chlorobenzenes (CBzs), chlorophenols (CPhs), and polyaromatic hydrocarbons (PAHs), caused a serious problem (Desroches-Ducarne et al. 1998b; Dong et al. 2002; Hu et al. 2013; Ni et al. 2009; Oh et al. 2007; Takaoka et al. 2003; Yang-Jing and Zhang 2011). Among all pollutants, PCDD/Fs are the most toxic ones.

Regarding the MSWIs used, three main types can be distinguished: a rotary kiln, a stoker, and a fluidized bed. And pyrolysis furnace is also suggested for waste thermal treatment. The stoker and circulating fluidized bed (CFB) are the most commonly used in China (Nie 2008). The stoker incinerators are favored due to their better suitability for MSW and simultaneously good environmental performance and low maintenance and operating costs (Nie 2008; Su et al. 2015). They are widely used internationally and are usually adopted by large and coastal areas in China because of the relative high investment and dependence on the foreign complexity and high technology (Nie 2008). For fluidized beds, additional coal is usually mixed with MSW to achieve complete combustion. The CFB technology has much lower capital and operating costs compared to the stoker incinerators and is more common in small- and mid-sized cities, as well as the larger cities in the middle and western China (Hai-yun 2010; Nie 2008).

In the past decades, following the rapid development and commercialization of the CFB incinerators across China, the number of studies focusing on PCDD/F emissions generated in different conditions was published, yet the results were widely varying (Desroches-Ducarne et al. 1998a; Dong et al. 2002; Van Caneghem et al. 2012; Yan et al. 2006). Moreover, less attention was drawn to the stoker incinerators installed in China compared to the incinerators operated abroad (Liu et al. 2013; Neuer-Etscheidt et al. 2006; Shin et al. 1999). Nowadays, the stoker incinerators have gained popularity in China, which is associated with the effects on CFB incinerators of the increasing coal price, poor stability of combustion, and amounts of fly ash disposal (Nie 2008; Tang et al. 2009; Xu 2009). Out of the studies published, the researches focused on the technical specifications of the incineration processes, such as energy efficiency and fuel consumption neglecting the environmental impact caused by the thermal conversion residues and air-borne emissions (Ning et al. 2013; Yang-Jing and Zhang 2011). At the same time, there is a significant difference between the emission levels of different incinerators (Gao et al. 2009), indicating the need to study the emissions from the stoke incinerators.

In addition to PCDD/Fs, a number of emissions, such as CBzs, CPhs, and PAHs, are generated during MSW incineration process at significant levels (Ghorishi and Altwicker 1995; Kilgroe et al. 1990; Oh et al. 2007; Takaoka et al. 2003). However, there are no limit values for the emission of CBzs, CPhs, and PAHs into atmosphere in China. Furthermore, certain emissions are significant precursors for PCDD/F generation (Altwicker et al. 1992; Ballschmiter et al. 1988; Ghorishi and Altwicker 1995) and show a good indication of near-online monitoring PCDD/Fs (Kato and Urano 2001; Lavric et al. 2005; Streibel et al. 2007; Xue-Feng et al. 2006; Yin et al. 2007). Furthermore, there is a lack of studies focusing on the emissions of CBzs, CPhs, and PAHs in China (Chen et al. 2016; Yan et al. 2010a, b).

This paper comparatively investigated the concentration of PCDD/Fs, CBzs, CPhs, and PAHs in the stack gas of two different municipal waste incinerators: a typical CFB incinerator and a stoker incinerator equipped with a novel air pollution control device, a selective catalytic reduction (SCR) technology first used in China. The concentration; congener profiles; and gas/particle distribution of PCDD/Fs, CBzs, CPhs, and PAHs were studied, and the results of the two different incinerators were compared and discussed. Finally, the relationship between the CBzs and PCDD/F formation, as a potential model for indication of PCDD/F emissions from the MSWIs, was discussed.

Materials and methods

The waste incinerators

Table 1 lists the basic information about the two MSWIs. MSWI A is located in a large waste-to-energy plant, with the most advanced air pollution control device (APCD). Waste is fed by two grab cranes to the incinerator from two separated waste pools. A Mitsubishi-Martin reverse reciprocating mechanical stoker furnace with a capacity of 750 t/day is used in the plant. After being fed into the incinerator, waste is dried, is burned, and finally becomes slag out. In this incinerator, waste mixed more efficiently, thus achieving high combustion efficiency. Auxiliary fuel is used when the calorific value of the waste is not sufficient to maintain the temperature of the furnace at the required level of 850–1050 °C. The methods of the APCD include a selective non-catalytic reduction (SNCR) system, a semi-dry scrubber, a dry scrubber, an activated carbon injection (ACI) line, a fabric filter, and a SCR system. It is worth noting that the MSWI plant is the first MSWI plant that uses SCR technology in China.

MSWI B is a circulating fluidized bed (CFB) incinerator with a capacity of 400 t/day. The incinerator type is typical for

Table 1 Characteristics of the studied MSWI plants located in China

	MSWI A	MSWI B
Facility type	Stoker	CFB
Capacity (t/day)	750	400
Furnace temperature (°C)	800–1050	750–900
Average oxygen content of in stack gas (%)	12.8–13.9%	13.7–17.5%
Rated evaporation capacity (t/h)	82.76	75
Air pollution control device	SNCR, semi-dry scrubber, dry scrubber, activated carbon injection, fabric filter, and SCR	SNCR, semi-dry scrubber, activated carbon injection, and fabric filter
Operation time	7 days a week and 24 h	7 days a week and 24 h

the majority of eastern cities in China. The APCD includes a SNCR system, a semi-dry scrubber, an ACI, and a fabric filter. It is a typical incinerator used in the most eastern cities in China.

Sample collection

In this study, ten samples from the stack of the MSWI A and eight samples from the stack of the MSWI B were collected. Each sampling lasted for 120–180 min to sample around 2–4 m^3 of gas. An isokinetic sampler (KNJ, Korea) was used for the sampling following the US EPA method 23a (EPA 1995), as described in detail by Chen et al. (2008). Each sample had two parts: the filter for the particle phase targets and the XAD-2 resin for the gas phase targets. The water collected in the sampling trains was analyzed for CBzs and CPhs. For the MSWI A, all ten samples were analyzed for PCDD/Fs and CBzs, five of them (samples 2–6) analyzed for the particle phase and the gas phase separately. For the MSWI B, all eight samples were analyzed for PCDD/Fs and CBzs and for the particle phase and the gas phase separately. CPhs and PAHs were also analyzed in all samples.

The samples collected were extracted stepwise with methylene chloride and toluene, and the extracts were concentrated separately to avoid losses of semi-volatile compounds (Neuer-Etscheidt et al. 2006; Oh et al. 2007). After the extraction, aliquots of the samples were taken for the analysis of the target compounds.

Sample treatment and analysis

The PCDD/F cleanup procedure and analysis were performed according to the US EPA Method 23a (EPA 1995). Identification and quantification of PCDD/Fs were performed by HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) coupled with a JMS-800D mass spectrometer (JEOL, Japan). A DB-5ms (60 m × 0.25-mm I.D., 0.25-μm film thickness) capillary column was used for the separation of the PCDD/F congeners.

The mean recoveries of standards for PCDD/Fs ranged from 55 to 125%, which are all within the acceptable range of 25–150%. The toxic equivalents (TEQ) were calculated using NATO/CCMS factors (Bhavsar et al. 2008). All the concentrations were normalized to dry air, oxygen content of 11%, pressure of 1.01×10^5 kPa, and temperature of 237 K. The TEQ values of PCDD/Fs were calculated with the international toxic equivalent factors (I-TEFs) according to the standard for pollution control at the municipal solid waste incinerators in China (Ministry of Environmental Protection of the People's Republic of China 2000).

The methodology for the pretreatment of CBzs is described in details by Yan (2012). GC-ECD (GC 6890N, Agilent,

USA) with a DB-5 column (30 m × 0.25 mm × 0.25 μm) was used to analyze CBzs.

The methodology for the pretreatment of CPhs is described in details by Huang et al. (2016). An Agilent 6460 triple quadrupole liquid chromatography/mass spectrometer (LC/MS) and a chromatographic column Zorbax XDBC8 (2.1 mm × 150 mm × 3.5 μm) were used to measure CPhs.

The cleanup procedure and the analysis method for PAHs were performed according to Method HJ 646-2013 and EPA Method 8270 using Agilent 6890N GC/5975B MSD.

Results and discussion

Stack gas emissions of PCDD/Fs

Ten stack gas samples from MSWI A and eight from MSWI B were collected and analyzed for PCDD/Fs. Five of MSWI A samples (samples 2–6) and all MSWI B samples were analyzed for particle phase and gas phase separately. The concentrations and I-TEQ values of PCDD/Fs from the stack gas of MSWIs A and B are shown in Fig. 1. The emissions of the MSWI A ranged from 0.011 to 0.109 ng international toxic equivalent (I-TEQ)/Nm^3, nearly all conforming to the current PCDD/F emission standard for MSWI in China (0.1 ng I-TEQ/Nm^3). On the contrary, the concentration of PCDD/Fs detected in the MSWI B at the level of 0.734 to 24.6 ng I-TEQ/Nm^3 exceeded the emission standard in most of the cases and revealed significant variation of emissions at the plant.

The substantial difference between the two results for the two MSWI plants can potentially be attributed to the different MSWs fed into the process and alternative furnace types applied and finally to the APCDs. The new stoker furnace of the MSWI A has higher combustion temperature and longer residence time for waste in the furnace, which together could result in more complete combustion of waste and better adaptability to complex waste in China, compared to the old CFB furnace. This is also indicated by the low concentration of carbon monoxide (13.5 mg/Nm^3) in the stoke furnace incinerator. Furthermore, the APCD used in MSWI A was more comprehensive and showed a better performance and especially obvious for NO_x in Fig. 2. The APCD in MSWI B, which was used for longer years than that in the new MSWI A, might not be well. Especially for the fabric filter, one of the MSWI Bs seemed to have some leakages according to the obvious dust in samples. The PM emission level was also unstable and high, compared with only 10 mg/Nm^3 of average emission level from MSWI A.

Table 2 shows the PCDD/F emission from the two incinerators studied and other MSWIs published during the past 10 years. It can be seen that the PCDD/F emission levels greatly varied in China, especially in fluidized bed incinerators. Different incinerator types affect the pollution emissions

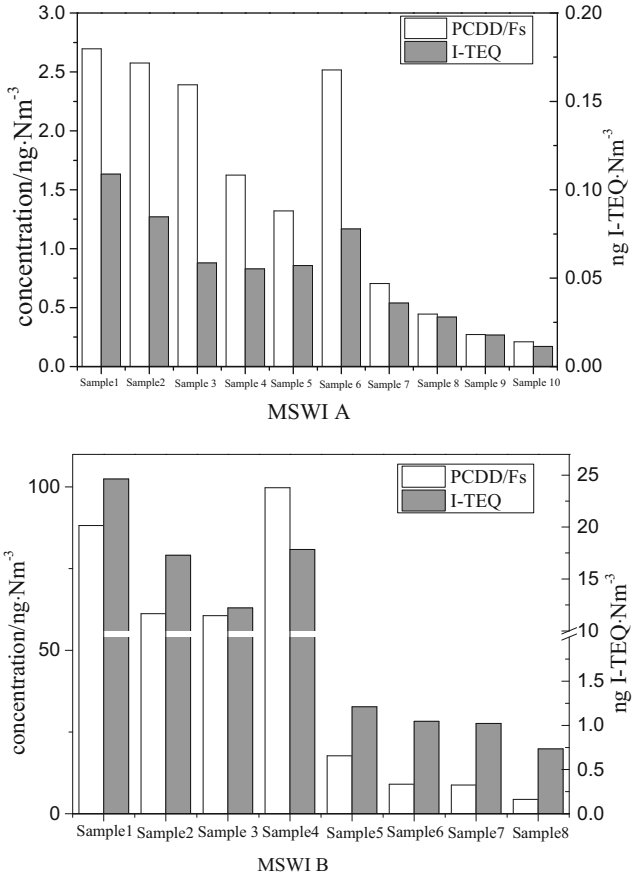

Fig. 1 The concentrations and I-TEQ of PCDD/Fs from stack gas of MSWIs A and B

significantly. The PCDD/F emissions from stoker furnace incineration plant are usually lower (Liu et al. 2013; Ni et al. 2009; Yang-Jing and Zhang 2011; Hung et al. 2016; Li et al. 2016), which is consistent with our results. However, also, fluidized bed incinerators can comply with 0.1 ng TEQ/Nm^3 through adequate flue gas cleaning technology and catalyst (Sakurai et al. 2003; Van Caneghem et al. 2012). The APCD system is an important factor especially in CFBs. The semi-dry scrubber, an activated carbon injection (ACI), and a fabric filter are commonly used, while the SCR and a dry scrubber are used seldom, yet such air pollution control system is a new type of the cleaning strategy used in the MSWI A and was advantageous in controlling the PCDD/Fs and other pollutant emissions. Proper APCDs with good maintenance help to decrease the PCDD/F emissions.

Distribution of PCDD/Fs

PCDD/F congener distribution

The congener profiles presented in this study are expressed in I-TEQ values. The I-TEQ contributions of 17 PCDD/Fs were

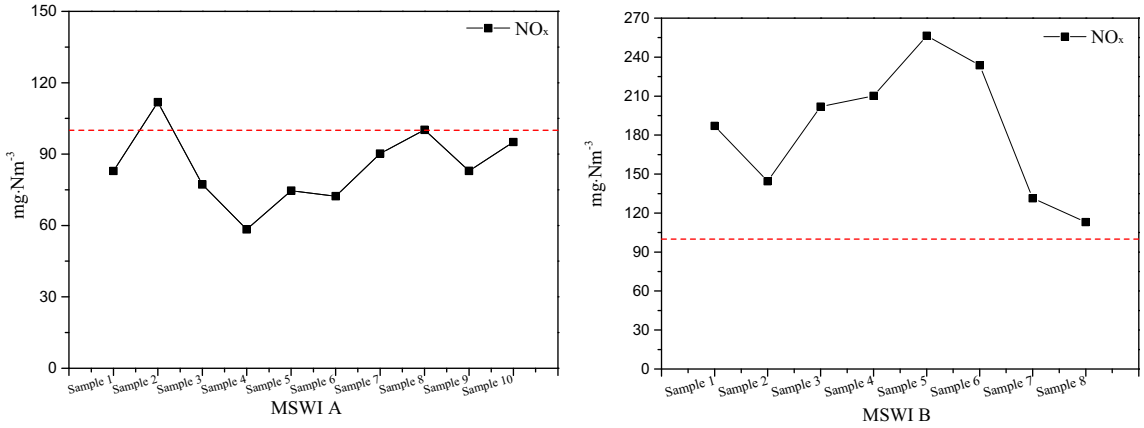

Fig. 2 The emissions of NO_x from MSWIs A and B during the sampling period

also calculated and are shown in Fig. 3. In this study, 2,3,4,7,8-pentachlorodibenzofuran (PeCDF) was the most abundant congener detected in the stack gas from MSWIs A and B accounting for 24.3–43.6 and 32.5–75.6% of the total I-TEQ values, respectively. The proportion of 2,3,4,7,8-PeCDF increased also with the increase of the I-TEQ value. Regarding the stack gas in the MSWI A, 2,3,4,6,7,8-hexachlorodibenzofuran (HxCDF), 1,2,3,6,7,8-HxCDF, and 1,2,3,4,7,8-HxCDF also together represented a significant fraction of PCDD/Fs. However, for the MSWI B, which had a high I-TEQ value, several PCDD congeners and low chlorine PCDFs were more obvious, such as 2,3,7,8-tetrachlorodibenzofuran (TCDF) (5.5–18.4%),1,2,3,7,8-PeCDD (4.4–8.9%), and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (4.4–18.2%). Studies (Gao et al. 2009) have concluded the three possible factors affecting the congener distribution of PCDD/Fs in incinerators: the types of incinerators, waste composition, and the types of APCDs.

Table 2 The PCDD/F emissions from the two incinerators studied and other MSWIs in the past 10 years in China

PCDD/F emissions (ng I-TEQ/Nm^3)	MSWI types	Capacity (t/day)	APCD	Reference
0.011–0.109	Stoker	750	SNCR, semi-dry scrubber + dry scrubber + ACI + fabric filter + SCR	This study
0.734–24.6	Circle fluidized bed	400	SNCR + semi-dry scrubber + ACI + fabric filter	This study
0.012	Fluidized bed	60–200	bag filter (BF)/ACI; catalyst	Sakurai et al. (2003)
0.071			BF/ACI	
0.26			BF/ACI	
1.41			BF	
4.05			BF	
0.0054–0.196	Fluidized bed incinerators	200–300	Semi-dry scrubber + BF	Yan et al. (2006)
0.008	Fluidized bed waste incinerators	/	Adequate flue gas cleaning technology	Van Caneghem et al. (2012)
0.001–0.01	Grate furnace			
0.026	Grate stoker	800	Semi-dry scrubber + ACI + fabric filter	Liu et al. (2013)
0.5	Grate stoker	200	Water screen duster, fabric filter	
0.042–2.46	Grate, fluidized bed incinerators	150–500	Semi-dry scrubber (+ activated carbon) + fabric filter	Ni et al. (2009)
0.39	Mechanical grate incinerator	450	Activated carbon + PTFE bag filters	Yang-Jing and Zhang (2011)
3.18	Circle fluidized bed	250		
0.042–0.065	Grate	600	SNCR, semi-dry absorption + ACI + BF	Hung et al. (2016)
0.118	Grate	800	Semi-dry scrubber + ACI + BF	Li et al. (2016)
0.0164	Grate	1050	Semi-dry scrubber + ACI + BF	
0.0186	Grate	800	Semi-dry Scrubber + ACI + BF	
0.0104	Grate	800	Semi-dry scrubber + ACI + BF	
0.00793	Grate	1050	Semi-dry scrubber + ACI + BF	
0.0819	Grate	1600	Semi-dry scrubber + ACI + BF	

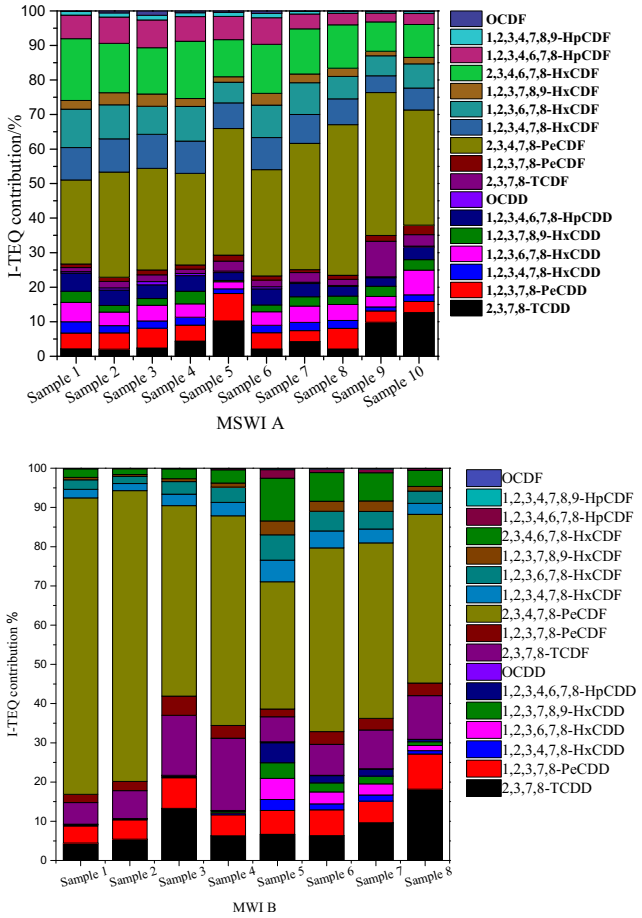

Fig. 3 The I-TEQ contributions of 17 PCDD/Fs from MSWIs A and B

PCDD/F homologue distribution

The homologue profiles of PCDD/Fs in the two MSWIs are shown in Fig. 4. Samples from the MSWI A had high fractions of HpCDD, octachlorodibenzodioxin (OCDD), and HpCDF, often exceeding 20%. Regarding the MSWI B, PeCDF had the highest concentration fraction of up to 55.1%. The rest important elements were TCDF and HxCDF. The distribution of PCDD/F emissions from the MSWI A was more uniform than that of MSWI B. MSWI B, as a CFB incinerator, has more complex control systems, and the lower combustion temperature was affected easily by moisture contents in waste, and shorter combustion time required higher pretreatment levels of waste. However, MSW has high moisture content and low calorific value in China. Furthermore, the overhaul of CFB furnaces is very frequent in China. Frequent startups and shut downs, changeable furnace temperature, and insufficient combustion could induce more complex formation reactions of PCDD/Fs and other persistent organic pollutants. Figure 4 for the MSWI B shows higher abundance of high-chlorinated PCDDs compared to the low-chlorinated PCDDs, while there was an opposite situation with PCDFs. It could be found that low-chlorinated PCDDs more often changed to high-chlorinated PCDDs, while high-chlorinated PCDFs more often dechlorinated to low-chlorinated PCDFs. It was difficult for low-chlorinated PCDFs to form high-chlorinated PCDFs. This is consistent with the previous studies (Altarawneh et al. 2009). The formation of PCDF isomers was controlled by dechlorination. Other PCDFs could be produced from OCDF, while PCDDs were not likely to be derived from the dechlorination of OCDD but from condensation of precursors and further chlorination of the gaseous PCDDs. PCDD/F emissions from MSWI A concentrated on both higher chlorinated PCDDs and PCDFs, while emissions from MSWI B concentrated on tetra- to pentachlorinated PCDFs. PCDDs were far less than PCDFs both in stokers and CFBs, ratios from 0.102 to 0.469.

Gas/particle distribution of PCDD/Fs

The gas/particle distribution of PCDD/Fs in the stack gas of the MSWIs A and B was investigated. The I-TEQ values of PCDD/Fs in the stack gas of the MSWI A were 0.052–0.078 ng I-TEQ/Nm^3 in the gas phase and 0.003–0.007 ng I-TEQ/Nm^3 in the particle phase. Considering the MSWI B, the values were 0.677–24.6 ng I-TEQ/Nm^3 in the gas phase and

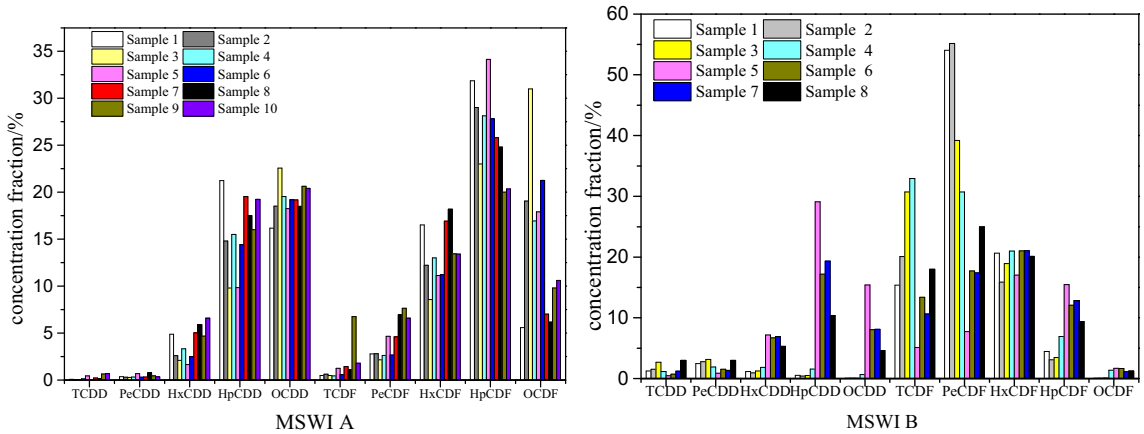

Fig. 4 The concentration fractions of PCDD/F homologue from the MSWIs A and B

0.034–0.298 ng I-TEQ/Nm^3 in the particle phase. For the MSWI A, the proportion in gas phase of the TEQ values was 92.2–94.7% and that of PCDD/F concentrations was 74.3–84.8%. The proportion in gas phase of both TEQ values and concentrations in the MSWI B ranged between 70 and 90%. The proportion in gas phase of TEQ values was higher than that of PCDD/F concentrations. This was related to the fact that PCDD/F congeners possessing high toxic equivalent factors (TEFs), namely 2,3,7,8-TCDD (TEF = 1) and 2,3,4,7,8-PeCDF (TEF = 0.5), mainly accumulating in the gas phase, had low concentrations but high TEQ values in samples of MSWI A. The research findings indicated availability of the majority of PCDD/Fs in the gas phase of stack gases from both the stoker and the CFB furnaces, as suggested by other researchers (Chang et al. 2004a; Chang et al. 2004b; Chi et al. 2005; Chi et al. 2006; Li et al. 2015).

The two gas particle partitioning models, namely the Junge–Pankow model (Edzwald and In 1977; Pankow 1994) and the octanol/air partition coefficient (K_{oa})-based model (Finizio et al. 1997; Harner and Bidleman 1998), are commonly used to explain the facts at present (Chao et al. 2004; Li et al. 2015; Oh et al. 2001). Temperature, particle concentrations, and chlorination levels might affect the gas particle partition of PCDD/Fs (Chang et al. 2004a, b; Chi et al. 2006; Li et al. 2015). Particularly, the increase of the cold vapor pressure, which facilitates the absorption of semi-volatile compounds on the particles surface, is associated with the rising temperature. Therefore, the gas-phase PCDD/Fs usually account for the majority of the PCDD/Fs detected in the stack gas of a MSWI plant, which generally has high temperature. Furthermore, the number of particles present in the stack gas decreases drastically after passing through efficient APCDs, thus inducing fewer particle-phase PCDD/Fs (Chang et al. 2004b; Li et al. 2015) (Fig. 5).

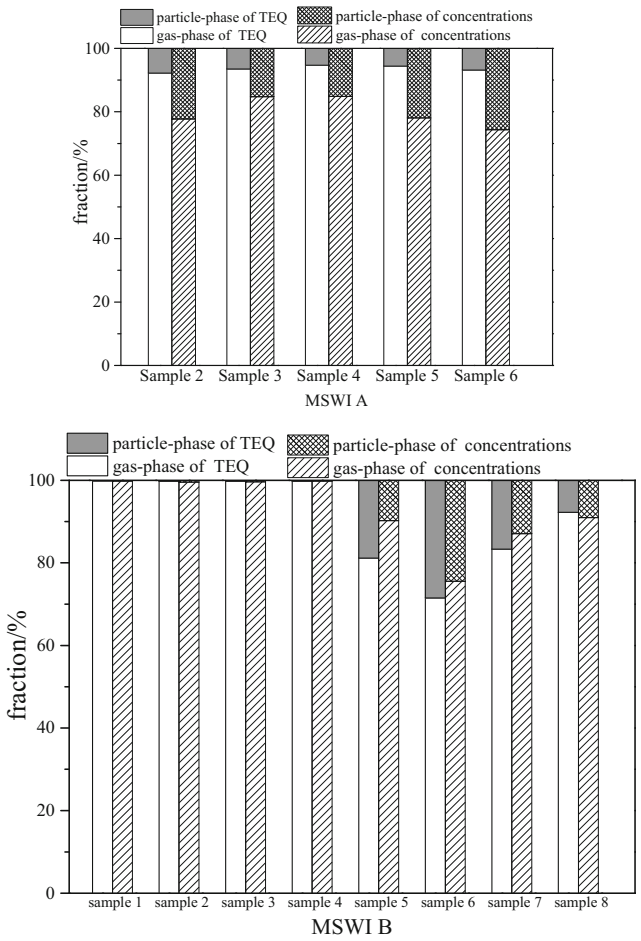

Fig. 5 Distribution of PCDD/Fs between particle phase and gas phase in the MSWIs A and B

Stack gas emissions of CBzs

The CBz emissions were also investigated in the study, and the results are shown in Table 3. The concentrations of dichlorobenzenes (DCBzs), trichlorobenzenes (TrCBzs), tetrachlorobenzenes (TeCBzs), pentachlorobenzenes (PCBz), and hexachlorobenzenes (HCBz) were high in the gas phase, whereas only few compounds could be detected in particle phase at the level mainly not exceeding 0.05 μg/Nm^3. The total concentration of CBzs detected at the MSWI A at the level of 0.05–3.2 μg/Nm^3 was much lower than the concentration detected at the MSWI B (10.9–75.1 μg/Nm^3), and other studies focused on the fluidized bed incinerators (Weber and Hagenmaier 1999). DCBz and PCBz accounted

Table 3 The concentrations of CBzs from stack gas of the MSWIs A and B

	DCBz	TrCBz	TeCBz	PCBz	HCBz	Total CBzs
MSWI A (μg/Nm^3)						
Sample 1	ND	ND	0.1	0.06	ND	0.16
Sample 2	1.2	0.2	0.4	0.09	ND	1.89
Sample 3	0.8	0.1	0.06	0.02	ND	0.98
Sample 4	0.2	ND	0.003	0.004	ND	0.21
Sample 5	0.4	0.07	0.03	0.05	ND	0.55
Sample 6	ND	0.03	0.01	0.005	ND	0.05
Sample 7	ND	0.06	0.04	0.05	0.001	0.15
Sample 8	ND	0.06	0.004	1.1	ND	1.16
Sample 9	ND	0.06	0.02	2.1	0.004	2.18
Sample 10	ND	0.08	0.02	3.1	ND	3.2
MSWI B (μg/Nm^3)						
Sample 1	14.3	16.0	15.3	2.1	2.6	50.3
Sample 2	22.1	0.4	16.0	0.7	0.6	39.8
Sample 3	15.2	5.6	9.9	0.8	0.44	31.9
Sample 4	27.8	16.7	12.1	8.3	2.6	67.5
Sample 5	7.1	5.1	1.2	0.3	0.12	13.8
Sample 6	5.3	3.9	1.2	0.4	0.11	10.9
Sample 7	22.0	30.3	15.1	6.5	1.2	75.1
Sample 8	21.0	19.4	11.6	6.4	1.2	59.6

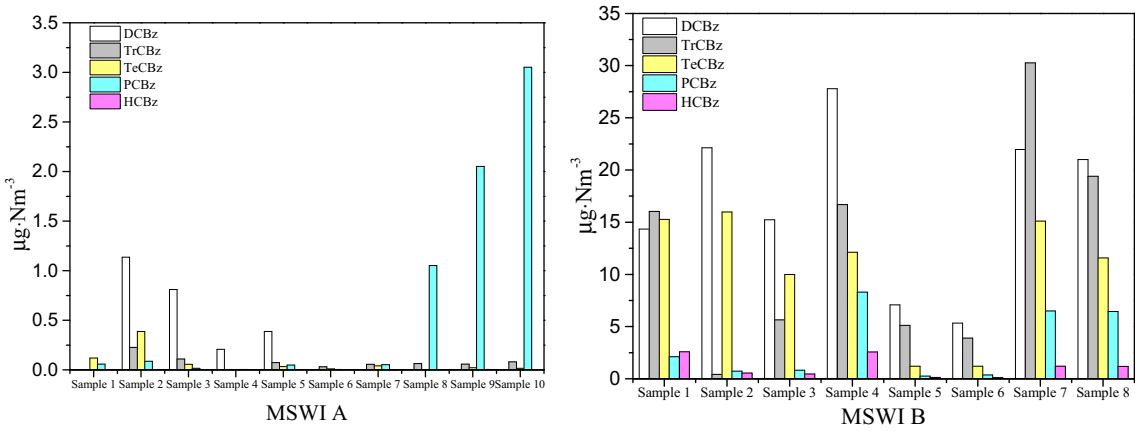

Fig. 6 The emissions of CBzs from stack gas of MSWIs A and B

for the majority of the CBz emissions from the MSWI A, whereas DCBz, TrCBz, and TeCBz dominated the CBz emissions from MSWI B as shown in Fig. 6. Guo (2014) suggested that the temperature caused by different furnaces seemed to be a primary factor affecting the concentrations of CBz, which was also supported in the present paper. The phase distribution of CBzs followed the distribution of the PCDD/Fs.

For the MSWI B, the isomers of the major CBz emissions, i.e., DCBz and TrCBz, were investigated and the results are shown in Fig. 7. In the previously published studies, 1,2,3-TrCBz and 1,2,3,4-TeCBz were the major compounds among all TrCBzs and TeCBzs, respectively (Guo 2014; Weber and Hagenmaier 1999; Weber et al. 2001). The concentrations of DCBz were rather low, even difficult to detect in most cases. The major pollutant of DCBzs, 1,2-DCBz, was still lower than 3 μg/Nm^3 (Weber and Hagenmaier 1999). In the present study 1,4-DCBz and 1,2,3-TrCBz were the major pollutants with the highest concentrations being 22.8 and 15.4 μg/Nm^3, respectively. The different results in the present study and previously published research might partly be explained by the different pretreatments of CBzs during the analysis. In the present study, a stepwise extraction, concentration, and pretreatment applied could together decrease the loss of low-chlorinated compounds promoting the possibility to obtain more accurate results for the concentrations of DCBzs.

The correlation between the PCDD/F and CBz emissions was investigated. The CBz emission level was usually 100–1000 times higher than the PCDD/F emissions, while similar emission trends for both emissions occurred. Therefore, the two factors, namely the higher emission level and similar emission trends, proved the possibility and convenience of indicating PCDD/F emissions through the analysis of the emissions of CBzs (Yan 2012). In this study, the I-TEQ value variation was compared with the major emissions of CBzs from the MSWI A (Fig. 8) and good correlations with TeCBz and PCBz emission concentrations in specific ranges were revealed (Fig. 9). For the MSWI A, when TeCBz concentration was in the range of 0.01–0.06 μg/Nm^3, TeCBz revealed a moderate positive correlation with I-TEQ value of PCDD/Fs (correlation coefficient $R^2 = 0.712$). When PCDD/F concentration was lower than 0.035 ng I-TEQ/Nm^3, PCBz revealed a negative correlation with PCDD/Fs, R^2 equal to 0.993. When the concentration of PCDD/Fs was higher than

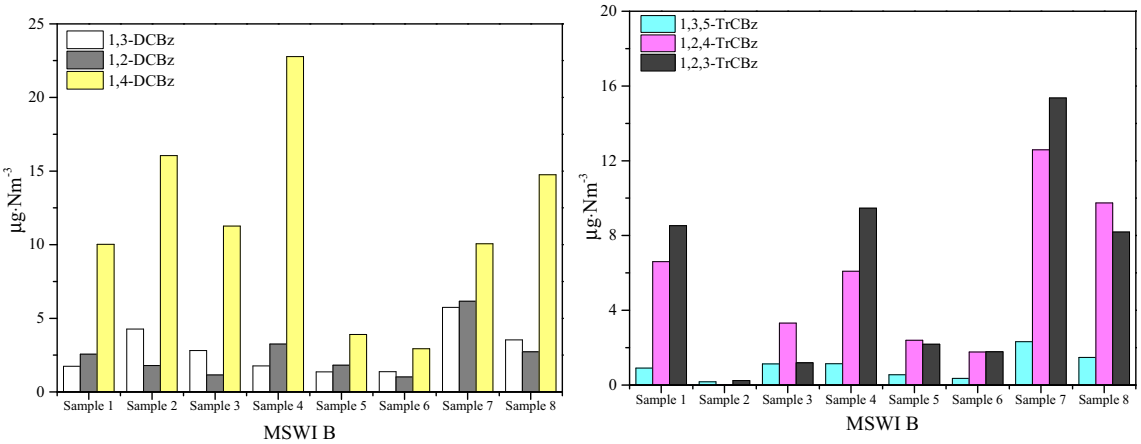

Fig. 7 The DCBz and TrCBz isomers from stack gas of MSWI B

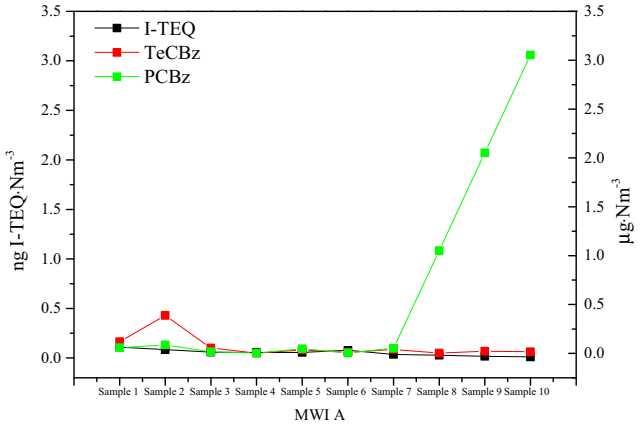

Fig. 8 The emission trends of PCDD/F I-TEQ values, TeCBz concentrations, and PCBz concentrations from MSWI A

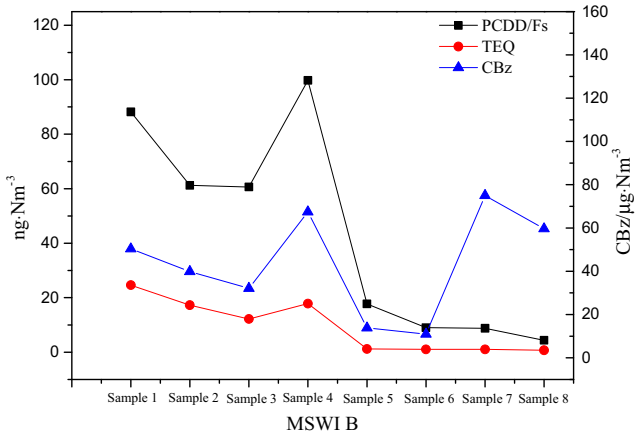

Fig. 10 The emission trends of PCDD/F concentrations, I-TEQ values, and CBz concentrations from MSWI B

0.050 ng I-TEQ/Nm^3, PCBz revealed a poor positive correlation (R^2 = 0.279). According to the eight samples from the MSWI B, the trend of the total CBz emissions was similar to the trends of both PCDD/F concentrations and I-TEQ values (Fig. 10).

Stack gas emissions of CPhs and PAHs

The stack gas emissions of CPhs and PAHs from the MSWI B were also investigated and are shown in Fig. 11. The sum of PAHs includes naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene. The total concentrations of CPhs and PAHs detected in the particle phase were extremely low, nearly 0.1–1% of the concentrations in gas phase, leading the following discussion towards the gas-phase emissions.

The total CPh concentration was 0.6–141.0 μg/Nm^3, half of results as high as the concentration at the boiler exit of one foreign stoker without the flue gas purification (Oh et al. 2007) and at the outlet of an electrostatic precipitator in a fluidized bed furnace (Weber and Hagenmaier 1999). The major pollutants were monochlorophenol (MCP), dichlorophenol (DCP), and tetrachlorophenol (TeCP), which were similar to the CPh distribution from the outlet of the wet scrubber reported by Takaoka et al. (2003). When the PCDD/F emission levels were high (samples 1–4), there were much more various chlorinated phenols.

PAHs are of a special interest due to their carcinogenicity and ubiquitous presence in the environment, forming a particular set of hydrocarbons, which are semi-volatile compounds containing two or more aromatic rings. Benzo[a]pyrene (BaP) is determined as the most toxic compound of PAHs. In this study, the total PAH and BaP concentrations of all eight stack samples were 148.6–4986.5 and 0.08–0.3 μg/Nm^3, respectively (Fig. 12). The results were extremely high compared with the PAH concentrations in the flue gas from a MSWI in normal condition (<50 μg/Nm^3) (Oh et al. 2007) and after several shut downs (210.9 μg/Nm^3) (Oh et al. 2007). Such emission level was similar to the level from old fluidized bed incinerators having unstable combustion (Weber et al. 2001). The total PAH concentrations could even be compared to the emissions from a medical waste incinerator (1290 μg/Nm^3) (Lee et al. 2002). Therefore, the results indicate that

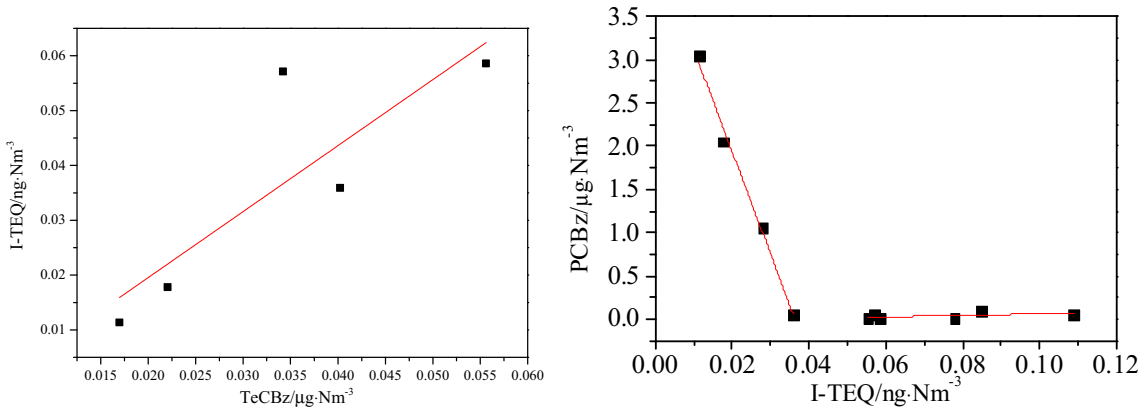

Fig. 9 The correlations between PCDD/Fs, TeCBz concentrations, and PCBz concentrations from the MSWI A

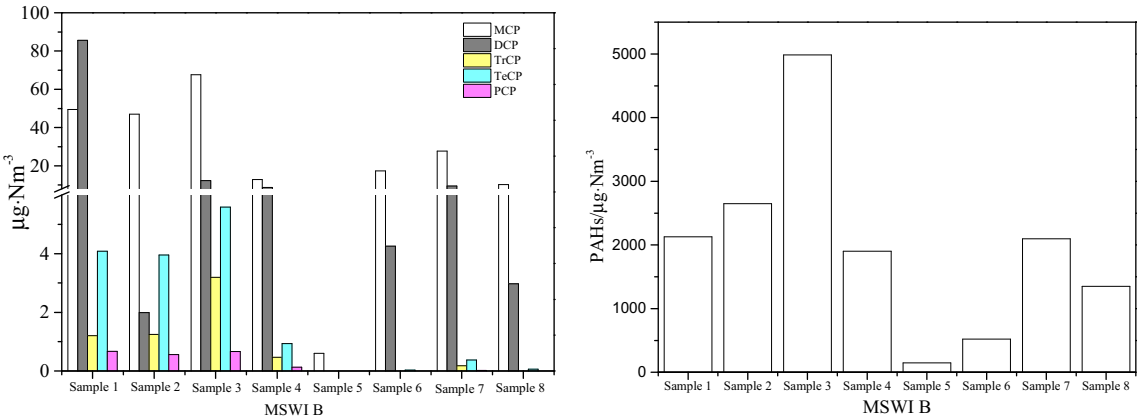

Fig. 11 The stack gas emissions of CPhs and total PAHs from the MSWI B

CPhs and PAHs are also significant pollutants detected at the waste incineration plants and required special attention. Particularly, the operation conditions of CFB incinerators had a significant impact on the pollution emissions.

Conclusion

The concentrations, homologue profiles, congener profiles, and gas/particle partition of PCDD/Fs and CBzs from stack gas of two different municipal solid waste incinerators were studied, and CPhs and PAHs from a CFB MSWI plant were detected.

For PCDD/Fs, the emission levels of the stoker MSWI plant equipped with the most advanced flue gas treatment technology in China ranged from 0.011 to 0.109 ng I-TEQ/Nm^3, nearly all conforming to the current PCDD/F emission standard for MSWI plants in China (0.1 ng I-TEQ/Nm^3). At the same time, the result of the CFB MSWI plant revealed unstable emissions of 0.734 to 24.6 ng I-TEQ/Nm^3, all exceeding the emission standard of China. However, both incineration emissions revealed an extremely high concentration of PCDD/Fs in the gas phase, above 90% of the total PCDD/F TEQ. 2,3,4,7,8-PeCDF (24.3–43.6% in MSWI A and 32.5–75.6% in MSWI B) was the most abundant congener of the stack gas from two incinerators. However, different congener and homologue distributions were observed due to different types of incinerators and APCDs.

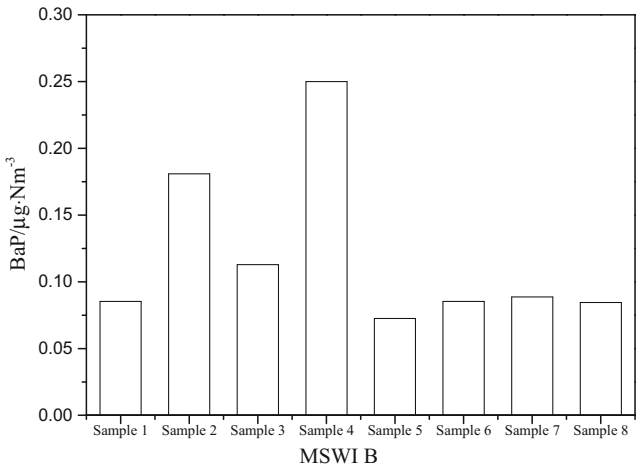

Fig. 12 The stack gas emissions of BaP from MSWI B

For CBzs, the total concentration detected at the MSWI A (0.05–3.2 μg/Nm^3) was much lower than concentration from the MSWI B (10.9–75.2 μg/Nm^3). The phase distribution of CBzs was the same as of the PCDD/Fs. Moreover, the CBz emission level was 100–1000 times higher than the PCDD/F emission level, while similar emission trends for both emissions occurred. The higher emission level and similar emission trends proved the possibility and convenience of CBz as indicators of PCDD/Fs. TeCBz revealed a moderate positive correlation with I-TEQ value of PCDD/Fs (R^2 = 0.712) when TeCBz concentration was in the range of 0.01–0.06 μg/Nm^3. And PCBz revealed a negative correlation with PCDD/Fs (R^2 = 0.993), when PCDD/F concentration was lower than 0.035 ng I-TEQ/Nm^3.

For CPhs and PAHs, high concentrations were detected in the stack gas from the MSWI B, 0.6–141.0 and 148.6–4986.5 μg/Nm^3, respectively. Several results were even as high as the concentrations at the boiler exit of one foreign stoker without a flue gas purification system. It was seen that CPhs and PAHs were significant pollutants generated at the waste incineration and, therefore, should be given much more attention in China.

Considering the emissions and the operation conditions of the two incinerators studied, the results underlined the importance of the proper maintenance of the waste incinerators in order to keep the pollution levels at the low-risk levels. Especially, fluidized bed incinerators require special attention in order to reach low emission levels of PCDD/F and other pollutants, even considerably lower than 0.1 ng TEQ/Nm^3.

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Compliance with ethical standards

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